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Mechanistic Insights into Catalytic Wet Peroxide Oxidation over Activated Carbons Treated with Sulfuric Acid

Helder T. Gomes[1,2], Sandra M. Miranda[2], Maria J. Sampaio[1,2], José L. Figueiredo[1], Adrián M.T. Silva[1], Joaquim L. Faria[1]*

[1] Laboratory of Catalysis and Materials, Associate Laboratory LSRE/LCM, Department of Chemical Engineering, Faculty of Engineering, University of Porto, Rua Dr. Roberto Frias, 4200-465 Porto, Portugal

[2] Department of Chemical and Biological Technology, School of Technology and Management, Polytechnic Institute of Bragança, Campus de Santa Apolónia, 5300-857 Bragança, Portugal

**: presenting author, email: htgomes@ipb.pt*

Introduction

The decomposition of hydrogen peroxide over activated carbons (AC) is known to proceed through the formation of hydroxyl radicals [1], which are very efficient oxidants in the degradation of organic pollutants. In a previous work, we found that AC treated with sulfuric acid are particularly efficient in the removal of Chromotrope 2R (C2R) by catalytic wet peroxide oxidation (CWPO) [2]. Now, we explore the role of surface groups with sulfur on the efficiency of AC in CWPO.

Experimental

Six AC samples characterized by different types and concentrations of sulfur containing functional groups, mainly thiol and sulfonic acids, were prepared by treatment of the commercial Norit ROX 0.8 with sulfuric acid. All samples were tested in the CWPO of 100 mg/L C2R aqueous solutions, performed at 50ºC, pH = 3, 0.5 g/L of catalyst and 34.6 mM of hydrogen peroxide.

Results and discussion

The results show that the AC treated with sulfuric acid have a superior performance in the removal of C2R than those non-treated, which should be ascribed to the presence of sulfur containing groups on their surface (namely to the presence of thiol and sulfonic acid groups) that contribute to the mechanism of pollutant removal with different functions. Sulfonic acid groups have a strong hydrophilic character, increasing the wetting of the materials in aqueous solution, thus increasing the corresponding adsorption of dissolved hydrogen peroxide. In turn, the presence of thiol groups is also fundamental due to their role in the efficient homolysis of the adsorbed hydrogen peroxide to generate hydroxyl radicals for further reaction with C2R, according to the following mechanism:

$$AC\text{-}SH + H_2O_2 \rightarrow AC\text{-}S + HO + H_2O \quad (1)$$
$$HO + H_2O_2 \rightarrow HO_2 + H_2O \quad (2)$$
$$AC\text{-}S + HO_2 \rightarrow AC\text{-}SH + O_2 \quad (3)$$
$$HO + C2R \ldots \rightarrow CO_2 + H_2O + \ldots \quad (4)$$

In the proposed mechanism, after adsorption of hydrogen peroxide molecules, hydroxyl radicals are generated by reaction between hydrogen peroxide and the reactive thiol groups, yielding thiyl radicals, eq. (1). The generated hydroxyl radicals may then react according to two competitive pathways. In the first alternative, with another hydrogen peroxide molecule, producing hydroperoxyl radicals, eq. (2), which may further interact with the oxidized AC surface, regenerating the catalyst and decomposing the radicals, eq. (3). Another alternative, the desired one, involves the reaction of the generated hydroxyl radicals with the pollutant, eq. (4), to yield degradation products. Following this mechanism it can be concluded that AC treated with sulfuric acid show increased efficiency in CWPO when compared with the non-treated due to the participation of sulfur containing surface groups on the adsorption/reaction mechanism.

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